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Experimental Study on Methane Production from Hydrate-Bearing Sandstone by Flue Gas Swapping

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Abstract:

Methane recovery from artificial hydrate-bearing sandstones by simulated flue gas swapping was tested using a core flooding experimental setup. Seven groups of experiments were conducted to investigate the effect of hydrate saturation as well as the initial porosity and permeability of sandstones on methane production and carbon dioxide capture. The results show that the CH₄ recovery efficiency and the amount of CO₂ captured increase with the increase of hydrate saturation at the same initial porosity and permeability of sandstone. The highest CH₄ recovery obtained is 51.6% and 99.4% of CO₂ in simulated flue gas is sequestered in the hydrate phase after swapping at 9.2 MPa and 277.15 K. Hydrate saturation was 82.5% and the initial porosity and permeability of sandstone are 25.1% and 49 mD, respectively. With the increase of initial porosity and permeability of sandstone, the CH₄ recovery efficiency and the amount of CO₂ captured increase when other

conditions (the hydrate saturation and reaction time) are similar. For investigating the CH₄-flue gas swapping mechanism, a micro-differential scanning calorimetry was used to test the heat changes in the whole reaction. No noticeable endothermic or exothermic phenomenon was detected in the CH₄-flue gas swapping, which indicates that CH₄ hydrate would form mixed hydrates directly instead of going through a dissociation and reformation process. Based on the observed experimental results, a CH₄-flue gas swapping mechanism is proposed and the reaction process is found to be essentially controlled by mass transfer.

1. Introduction

Gas hydrates are ice-like crystalline compounds in which guest molecules (such as CH₄, CO₂, N₂) are closed in cages formed by hydrogen-bonded water molecules under favorable thermodynamic conditions of low temperature and high pressure. Although the hydrate cage lattice can be combined in various ways, only three main types of structures are found in nature: structure I (sI), structure II (sII), and structure H (sH).¹ Gas hydrate formation is regarded as a serious problem in the petroleum industry since it can induce plugging in pipeline transportation and cause enormous economic losses; therefore, numerous studies have been conducted to address this issue.² On the other hand, naturally occurring gas hydrates have been perceived as a promising alternative energy source due to their giant storage in offshore sediments and permafrost regions. It has been reported that the amount of CH₄ stored in gas hydrates is twice the amount of carbon found in all fossil fuels worldwide.³⁻⁵

How to safely and efficiently recover CH₄ from natural gas hydrates remains a pressing challenge, in recent years, CH₄-CO₂ swapping has been seen as a potential approach which has certain advantages over other technologies that derive from conventional oil and gas industry to be used for gas hydrate exploitation, such as thermal stimulation,⁶⁻¹¹ depressurization,¹²⁻¹⁷ chemical inhibitor

stimulation.¹⁸⁻¹⁹ Because this method is a non-destructive way of substituting CH₄ molecules in the hydrate cage with CO₂ molecules, a geological event can be avoided during production. In addition, the direct use of flue gas (around 20 mol% CO₂ and 80 mol % N₂) instead of pure CO₂ can significantly enhance CH₄ recovery and save extra CO₂ separation cost before injection.²⁰ For investigating the CH₄-flue gas swapping mechanism, researchers have conducted their studies from thermodynamic,²¹⁻²³ microscopic,²⁴⁻²⁶ and kinetic perspectives.²⁷⁻³⁰ Lee et al.^{20,31-33} did a series of studies on CH₄-flue gas swapping, where they found that the maximum CH₄ recovery efficiency achieved are 84% and 90%, respectively, for sI and sII or sH gas hydrate. In addition, the first field test by swapping was conducted on Alaska North Slope in 2012: CH₄ was successfully produced several days after injecting flue gas into the hydrate-bearing sandstones.³⁴⁻³⁶ However, it is necessary to further investigate the CH₄-flue gas swapping before proceeding with large-scale commercial exploitation using this technology, because the CH₄ productivity is affected by many factors such as the hydrate saturation, the mass and heat transfer properties of the hydrate-bearing sediments, as well as the swapping reaction rate.

In previous work, we performed preliminarily investigations to ascertain the swapping behavior of CH₄ hydrate-bearing sandstone by injecting pure CO₂ and (CO₂+N₂) binary mixtures with different compositions using a core flooding experimental apparatus. Around 46% of CH₄ was produced from its hydrate phase after swapping with (CO₂+N₂) for 342 hours, the CH₄ recovery efficiency is lower than stoichiometric.³⁷ For the hydrate-bearing sandstones, the CH₄-flue gas swapping is significantly different from that in bulk phase. The CH₄-CO₂ swapping method adopted in our previous study was limited by CO₂ concentration where the residual free CH₄ (which is used to keep the CH₄ hydrate from dissociation) decreased the reaction driving force. In this study, this limitation was addressed by performing experiments where firstly the flue gas is injected continuously into the reactor to purge the free methane at a constant pressure and then pressurize it

to a certain value to start the swapping reaction at a high driving force. Since the exchange performance is sensitive to the mass transfer properties of hydrate-bearing sandstones, this work mainly focuses on how the porosity and permeability of sandstone affect the CH₄ recovery in the CH₄-flue gas swapping. The results can provide basic research information for natural gas hydrates exploitation by flue gas swapping.

2. Experimental Section

2.1. Apparatus.

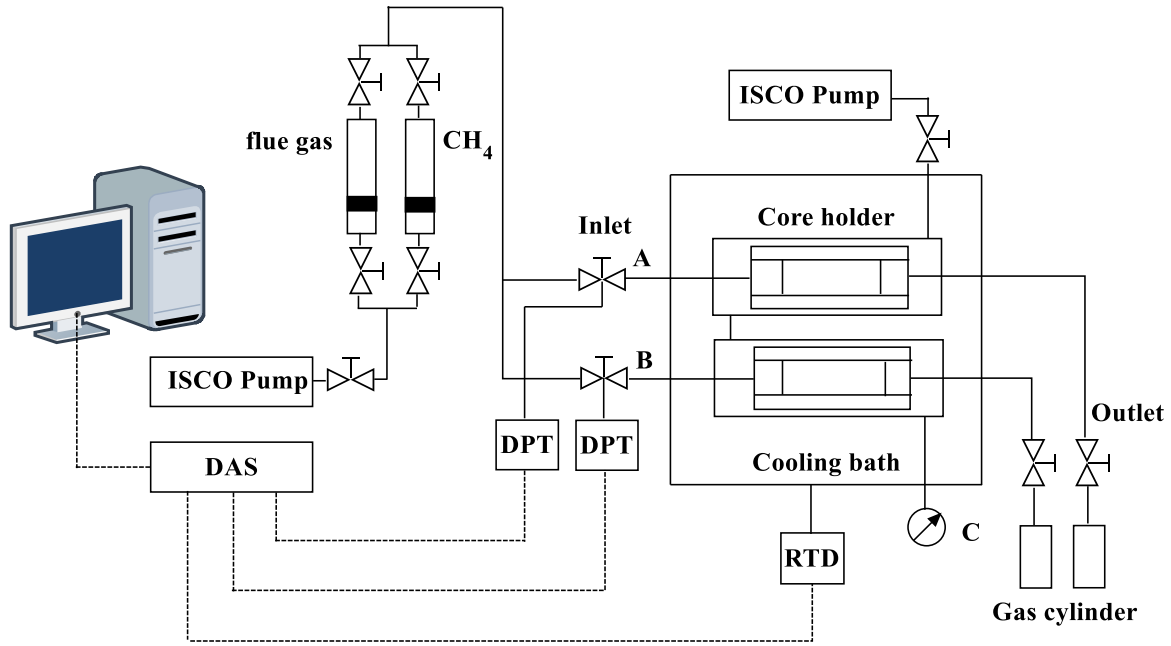


Figure 1. Schematic diagram of the experimental apparatus: RTD, resistance thermocouple detector; DPT, differential pressure transducer; and DAS, data acquisition system.

This study examined the CH₄ recovery from hydrate-bearing sandstones by injecting simulated flue gas. A schematic diagram of the experimental setup is shown in Figure 1. The principal parts of the setup are two core holder cylinders with an effective volume of 500 cm³ each, and the maximum

working pressure is 20 MPa. The two core holders are installed in a cooling bath in which a secondary platinum resistance thermometer (type-Pt 100) was used to monitor the temperature. The CH₄ and flue gas can be injected into the reactor from the injection cylinders with an electrical ISCO pump. When the swapping reaction was finished, the equilibrium gas can be released through two back-pressure regulators into two gas collection cylinders. The changes of pressure and temperature were collected by the pressure and temperature transducers and recorded in computer. A detailed introduction of the apparatus can be found in our previous publication.³⁷

2.2. Materials.

CH₄ (99.99%), CO₂ (99.99%) and N₂ (99.99%) were purchased from AGA Gas Company. The simulated flue gas containing CO₂ (19.2 mol%) and N₂ (80.8 mol%) was prepared by us, the composition of gas mixtures was analyzed by an Agilent gas chromatograph (GC 7890A). NaCl solution (3.35 wt%) was made in the laboratory. The characteristics of sandstones (originated from Germany) are listed in Table 1.

Table 1. Physical Properties of Sandstones used in This Study

Sandstone	Diameter (cm)	Length (cm)	Dry weight (g)	D _g (g·cm ⁻³)	D _b (g·cm ⁻³)	Porosity (%)	Permeability (mD)
A	2.55	7.77	73.76	2.48	1.86	25.1	49
B	2.55	7.77	79.22	2.56	2.00	22.0	44
C	2.55	7.77	82.70	2.57	2.08	19.1	37
D	2.55	7.77	85.03	2.60	2.15	17.5	31

*D_g and D_b are the grain density and bulk density, respectively. The porosity and permeability are measured by a steady state gas permeameter and porosimeter, the permeability reported here is Klinkenberg permeability.

2.3. Method.

2.3.1. Experimental Procedure.

The detailed description of experimental procedure has been reported in our previously study,³⁷ here we briefly introduce it as follows: first, the sandstones were cleaned (with toluene and ethanol) and dried, then saturated with brine water and installed into the apparatus. The cooling bath temperature was set to 277.15 K, then injecting CH_4 to start the reaction. CH_4 hydrate formation can be identified from a sudden pressure drop as shown in Figure 2. After preparing the hydrate-bearing sandstones, the sweep method⁵¹ was used to purge the free CH_4 then pressurize it to 9.0 MPa with flue gas to start the swapping reaction. One thing to note is that, in order to avoid CH_4 dissociation in this process, the reactor pressure should be always slightly higher than the equilibrium pressure of CH_4 hydrate at 277.15 K. The flue gas was replenished for improving the CH_4 recovery. After the swapping experiment was finished, the equilibrium gas was analyzed by GC. Typical pressure and temperature changes in the CH_4 -flue gas swapping was shown in Figure 3.

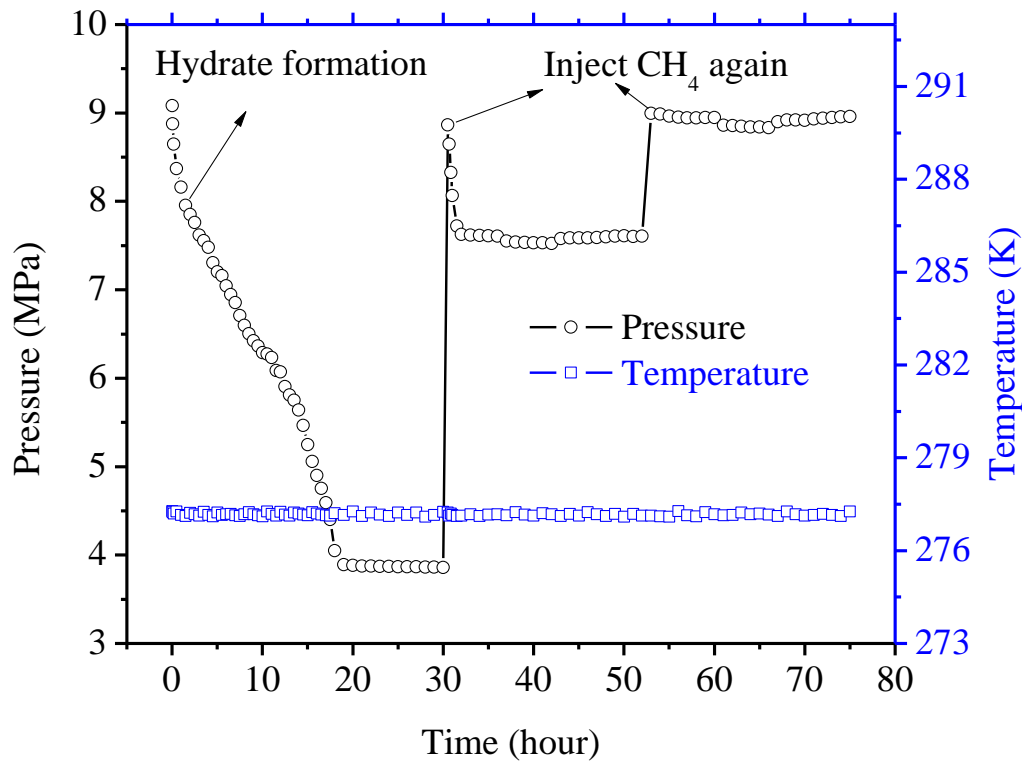


Figure 2. Pressure and temperature changes in CH_4 hydrate formation.

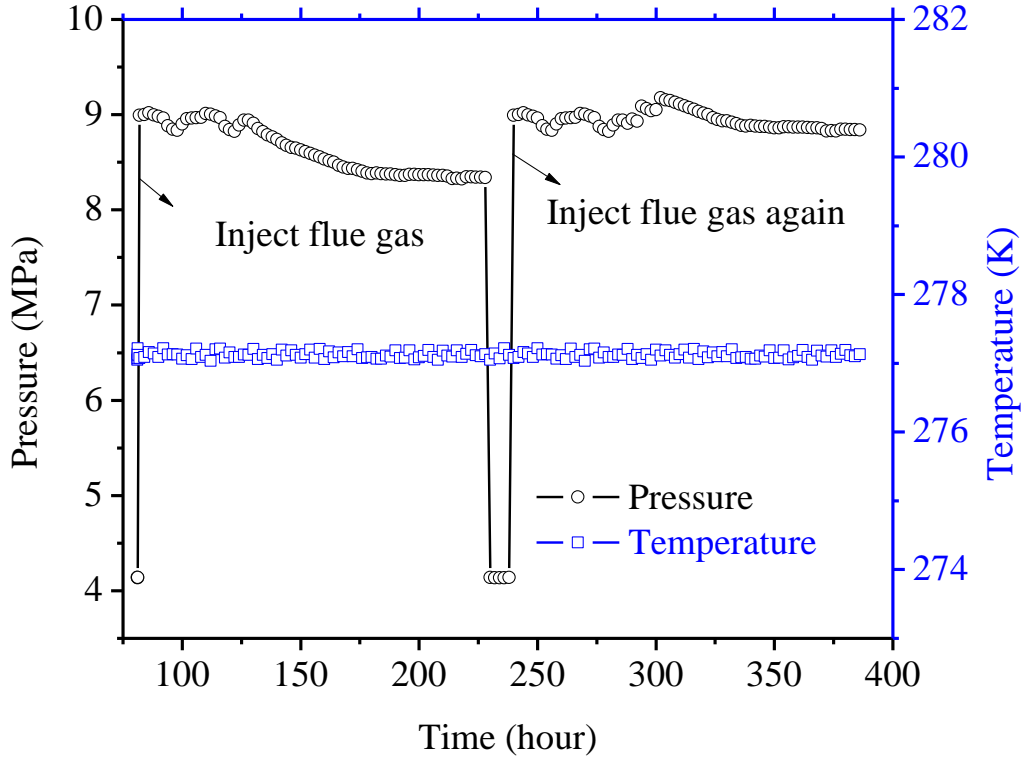


Figure 3. Pressure and temperature changes in CH₄-flue gas swapping.

2.3.3. Data Processing.

The mole number of CH₄ trapped in hydrate phase ($n_{\text{CH}_4,\text{H}}$) can be calculated by:

$$n_{\text{CH}_4,\text{H}} = \frac{\Delta PV}{ZRT} \quad (1)$$

Where ΔP is the pressure changes in CH₄ hydrate formation, V is the effective gas phase volume of the reactor, Z is the compressibility factor and can be calculated by BWRS equation of state,³⁸ R is the universal gas constant, T is the cooling bath temperature. The changes of dissolved gas in water phase at different pressures can be calculated by Henry's law, however, it can be ignored here since less water existed in the sandstones. The amount of water converted to hydrate can be calculated with a hydrate number 6.0,³⁹ then the corresponding water saturation (S_w), hydrate saturation (S_H) and gas saturation (S_G) can be obtained. Similarly, the mole number of CH₄ recovered ($n_{\text{CH}_4,\text{Re}}$) as well as CO₂ or N₂ captured ($n_{\text{CO}_2,\text{H}}$, $n_{\text{N}_2,\text{H}}$) in the swapping process can also be determined by

equation (1) when obtained the composition of equilibrium gas from GC as well as the pressure changes in reaction. The CH₄ recovery efficiency is defined as:

$$R_{\text{CH}_4} = \frac{n_{\text{CH}_4, \text{Re}}}{n_{\text{CH}_4, \text{H}}} \times 100\% \quad (2)$$

The detailed calculation procedure can refer to our previous articles.³⁷

3. Results and discussion

3.1. Properties of synthesized hydrate-bearing sandstones.

Based on the location of hydrate layer as well as the free gas and water, there are mainly three typical hydrate reservoirs in nature:⁴⁰ Class 1, hydrate layer located underneath two-phase zone of free gas and water; Class 2, hydrate layer formed under one-phase zone of free water (no gas); Class 3, hydrate layer with no free fluids coexisting. Class 1 is theoretically the most suitable for hydrate exploitation, since it is thermodynamically close to the hydrate equilibrium condition. However, the CH₄-flue gas swapping for the Class 1 and 2 would be not easy because the flue gas will firstly form new hydrates with the free water and affect the reaction rate. Therefore, we mainly synthesized hydrate samples resembling the situation in Class 3 in this work, focusing on how hydrate saturation as well as the initial porosity and permeability of sandstone affect the CH₄ recovery in swapping. The properties of the synthesized hydrate-bearing sandstone samples are listed in Table 2, and the sandstones A, B, C and D used here have the same cross-sectional area and length. In this study, we prepared the CH₄ hydrate-bearing sandstones with different hydrate saturations: (i) the higher hydrate saturation case (Run 1, 2, 5, 6, 7), where an annealing process was used to improve water conversion. This is done by raising and lowering the experimental temperature repeatedly, making sure the gas hydrates experience at least one cycle of dissociation and re-formation. The pressure and temperature curves measured during the annealing process in experimental run 2 and 1 are plotted in Figure 4 and 5, respectively, which correspond to two

different cases in the annealing process. As shown in Figure 4, the pressures have little difference before and after annealing, which suggests no more extra hydrate formed and redistributed in experimental run 2. However, Figure 5 shows that the system pressure after the annealing process falls to a lower value than before, which indicates more methane molecules trapped in the hydrate phase in the case of experimental run 1. It can be seen that the annealing process enhances the overall hydrate formation yield. One reason for this may be the inhomogeneous initial hydrate distribution in the sandstone where there is an amount of free water remaining unreacted in the first hydrate formation process. The annealing process dissociates and reforms the hydrate thereby increasing water conversion. In addition, the pressure and temperature curves of Run 5, 6 and 7 are more like Figure 4 (which is the case of Run 2), the reason might be that the hydrate saturation of sandstones in Run 5, 6 and 7 are basically the same with that in the Run 2. (ii) Experiments were also performed with a lower hydrate saturation (Run 3 and 4) case, in which only the initial CH₄ hydrate formation was performed and an annealing was not conducted.

Table 2. Properties of Synthesized CH₄ Hydrate-bearing Sandstones

Run	Sandstone	Temperature (K)	Pressure* (MPa)	$m_{\text{H}_2\text{O}}$ (g)	$n_{\text{CH}_4, \text{H}}$ (mmol)	S_{W} (%)	S_{H} (%)	S_{G} (%)
1	A	277.15	9.04	7.05	59.6	6.3	82.5	11.2
2	A	277.15	9.13	7.02	53.0	13.3	73.7	13.0
3	A	277.15	9.14	7.03	44.5	22.9	61.8	15.3
4	A	277.15	9.14	7.08	34.7	34.4	48.2	17.4
5	B	277.15	9.12	7.01	52.3	14.0	72.4	13.6
6	C	277.15	9.07	6.99	41.0	13.9	72.6	13.5
7	D	227.15	8.93	6.98	52.4	13.6	72.8	13.6

*The initial pressure after injecting CH₄.

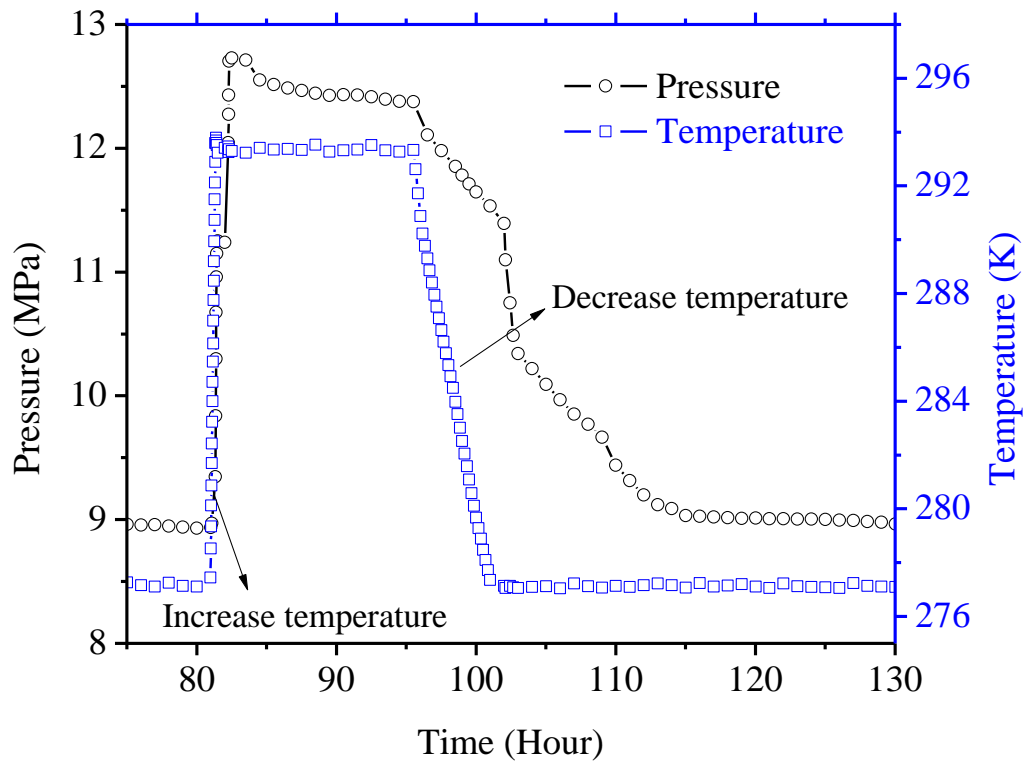


Figure 4. Pressure and temperature changes during the annealing process in experimental run 2.

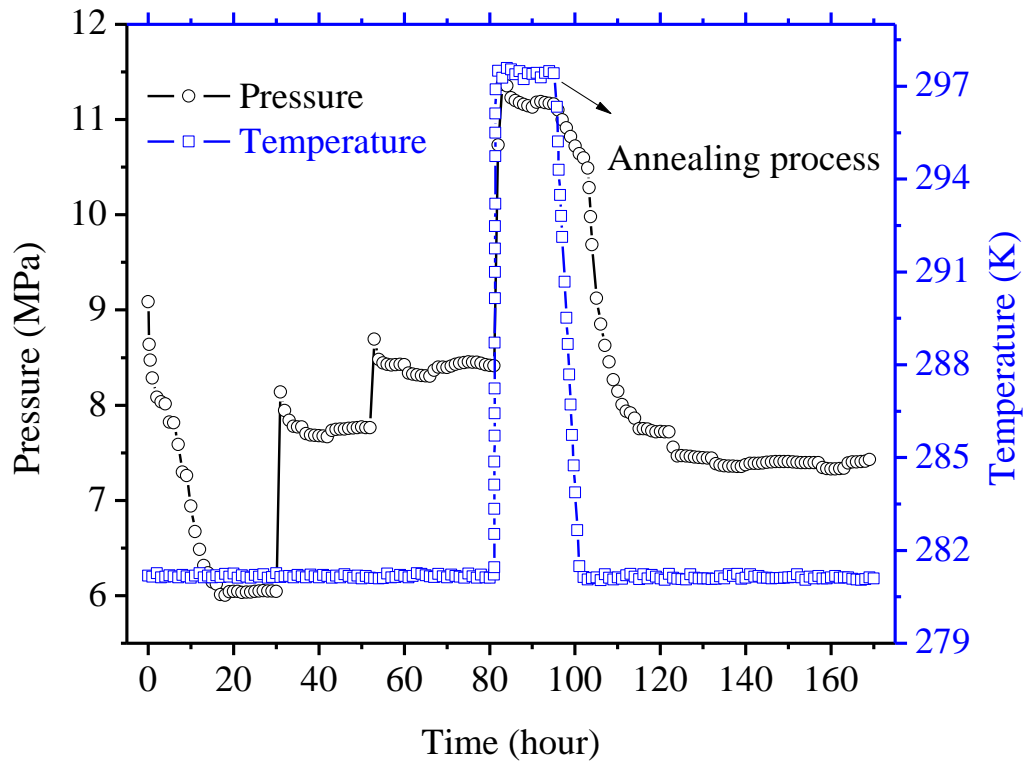


Figure 5. Pressure and temperature changes during the annealing process in experimental run 1.

3.2. The effect of hydrate saturation on the swapping process.

For studying the swapping behavior of flue gas in CH₄ hydrate-bearing sandstones, seven tests were conducted and the results are listed in Table 3. In this work, we used the same sandstone (A) to form gas hydrate four times to test the influence of hydrate saturation on the CH₄ recovery efficiency in the swapping process in order to ensure the same initial porosity and permeability. It has been reported that Alaska site test is distinguished by a higher hydrate saturation (around 75%),⁴¹ therefore the sample in Run 2 was prepared with similar hydrate saturation. From the properties of synthesized methane hydrate-bearing sandstone samples, it can be seen that the low S_H system has a relatively large amount of free water, and the water saturation in hydrate-bearing sandstones samples increases with the decreasing of hydrate saturation. Some researchers^{29,51} believe that the excess water in the system can affect the replacement reaction rate and lower the mass transfer efficiency since it causes the formation of (CO₂+N₂) mixed gas hydrates. In our study, it was observed that the CH₄ recovery efficiency increases with increasing hydrate saturation when other experimental conditions are similar, as shown in Figure 6. In addition, the amount of CO₂ captured also increases with increasing hydrate saturation, which suggests that there are more CO₂ molecules replacing CH₄ in hydrate cages under high hydrate saturation conditions. The reason for the results might be that, there are less free water in the sandstones with a higher hydrate saturation, which makes the CO₂ molecules can more immediately swap with CH₄ molecules in the hydrate phase. In the case of lower hydrate saturation sandstones, the CO₂ molecules probably first form new CO₂ hydrate with free water, which would increase the mass transfer resistance to some extent. Although the reaction with free water can consume a portion of CO₂ and increase the amount of CO₂ capture, it would decrease the concentration of CO₂ in gas phase and cannot contribute to increasing the CH₄ recovery efficiency. Here we obtained the highest recovery efficiency of 51.6%

at a hydrate saturation of 82.5%, about 99.4% of CO₂ in simulated flue gas is sequestered in the hydrate phase after swapping. This result is very close to the result in Lee's work,²⁷ where they test the CH₄-flue gas swapping with a one-dimensional reactor and the CH₄ recovery efficiency is 49%.

Table 3. Experimental Conditions and Results for CH₄-flue gas Swapping

Run	Sandstone	Temperature (K)	Pressure* (MPa)	$n_{\text{CH}_4,\text{Re}}$ (mmol)	$n_{\text{CO}_2,\text{H}}$ (mmol)	$n_{\text{N}_2,\text{H}}$ (mmol)	R_{CH_4}
1	A	277.15	9.18	30.8	20.4	10.4	51.6
2	A	277.15	9.08	26.4	19.9	8.6	49.7
3	A	277.15	9.14	21.0	16.1	6.9	47.1
4	A	277.15	8.94	16.1	15.4	2.6	46.3
5	B	277.15	9.05	24.5	19.6	6.6	46.8
6	C	277.15	8.98	22.4	17.9	5.7	42.9
7	D	227.15	8.98	21.5	15.9	4.5	41.0

* The equilibrium pressure after flue gas swapping.

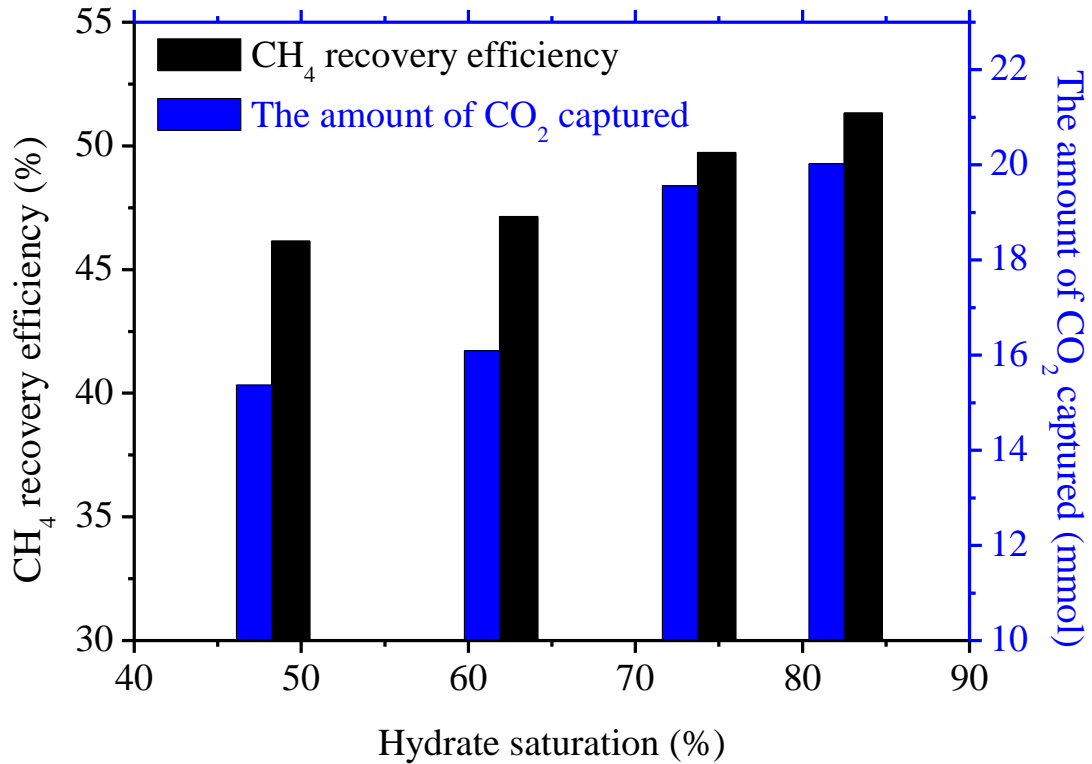


Figure 6. Methane recovery efficiency and the amount of CO₂ captured at different hydrate saturation.

3.3. The effect of porosity and permeability on the CH₄-flue gas swapping process.

To investigate how the porosity and permeability of sandstone affect the methane production and CO₂ capture during the swapping reaction, four tests were performed at the condition of identical hydrate saturation (around 73%). The porosity of sandstones A, B, C and D used here (corresponding to experimental run 2, 5, 6 and 7, respectively) are 25.1%, 22.0%, 19.1% and 17.5%, their permeability are 49, 44, 37 and 31 mD, respectively. One thing to note is that the porosity and permeability of sandstone in this work refer to that of the original sandstones, since it is difficult to measure that of the hydrate-bearing sandstones. Our previous experimental investigation showed that the CH₄-CO₂ swapping reaction process in hydrate bearing sandstones is significantly affected by the mass transfer of diffusion and the driving force.³⁷ Since the diffusion efficiency and driving force for the swapping reaction mainly depend on the CO₂ concentration gradient in the gas and hydrate phase, the decreasing CO₂ concentration with elapsed time during the swapping process would lower the mass transfer efficiency and reaction rate. In view of this situation, the limitations in mass transfer and replacement efficiency were addressed by many researchers by injecting swapping gas continuously to maintain a high CO₂ concentration in the system and keep a constant driving force,²⁷ however, this method to some extent would inevitably lead to CO₂ emission and increase gas recycling and separation cost in field scale production. In this work, we used a batch operation method that uses the flue gas to purge the free CH₄ before starting each swapping experiment, then replenishing the reactor with fresh flue gas once the reaction was assumed to be stopped due to lack of a driving force. The swapping process of experimental run 2, 5, 6 and 7 lasted 240 hours in all, after which the equilibrium gas was sampled and analyzed, the experimental results are shown in Figure 7 and 8, respectively. From Figure 7, it can be seen that the CH₄ recovery efficiency and amount of CO₂ captured increases with increasing sandstone porosity, which indicates that a higher porosity is beneficial to mass transfer and gas production. The effect

of permeability on CH₄ recovery efficiency and amount of CO₂ captured has the same trend. These results confirmed that the sandstone's porosity and permeability are important influence factors in CH₄-flue gas swapping. Figure 9 compares the CH₄ productivity in each experimental run, here it is the CH₄ average production rate per hour. It can be seen that, methane production rate decreases as the permeability decreases (the permeability of sandstones in run 2, 5, 6 and 7 are 49, 44, 37 and 31 mD, respectively). Especially, run 2, which has the highest permeability, resulted in a methane production rate 7.8-22.9% higher than that of runs 5, 6, and 7. In addition, the methane productivity also present a decreasing trend with decreasing hydrate saturation (the hydrate saturation of sandstones in run 1, 2, 3 and 4 are 82.5%, 73.7%, 61.8% and 48.2%, respectively).

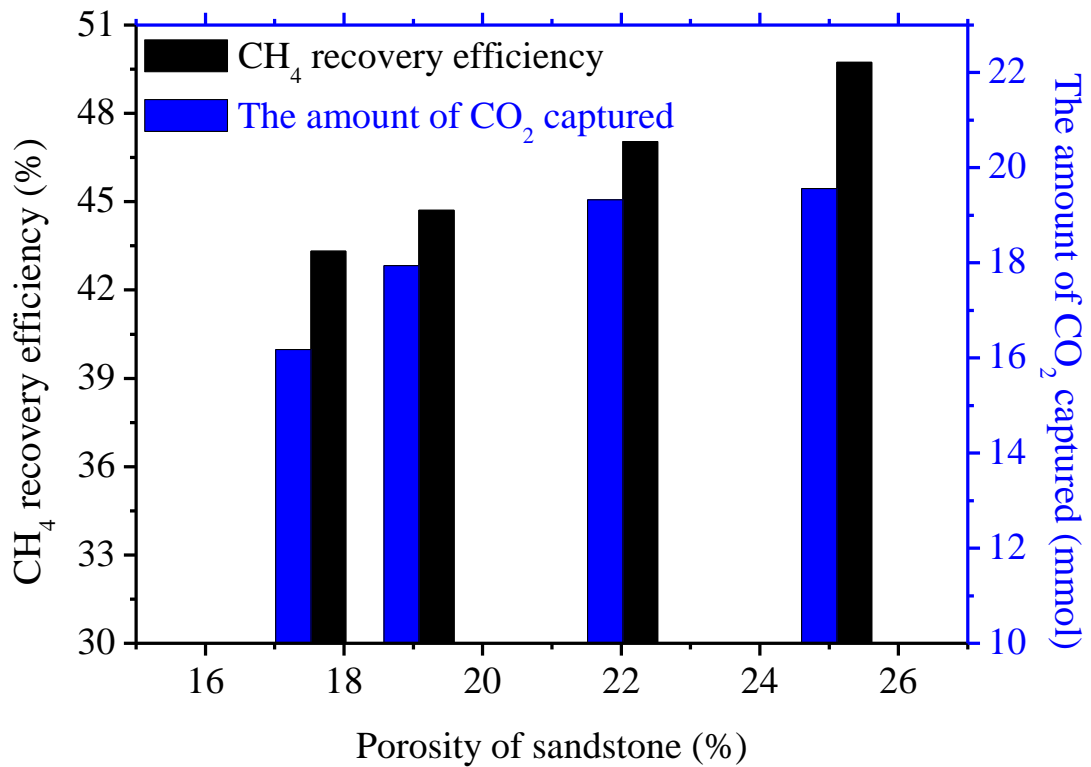


Figure 7. Methane recovery efficiency and the amount of CO₂ captured at different porosity of sandstones.

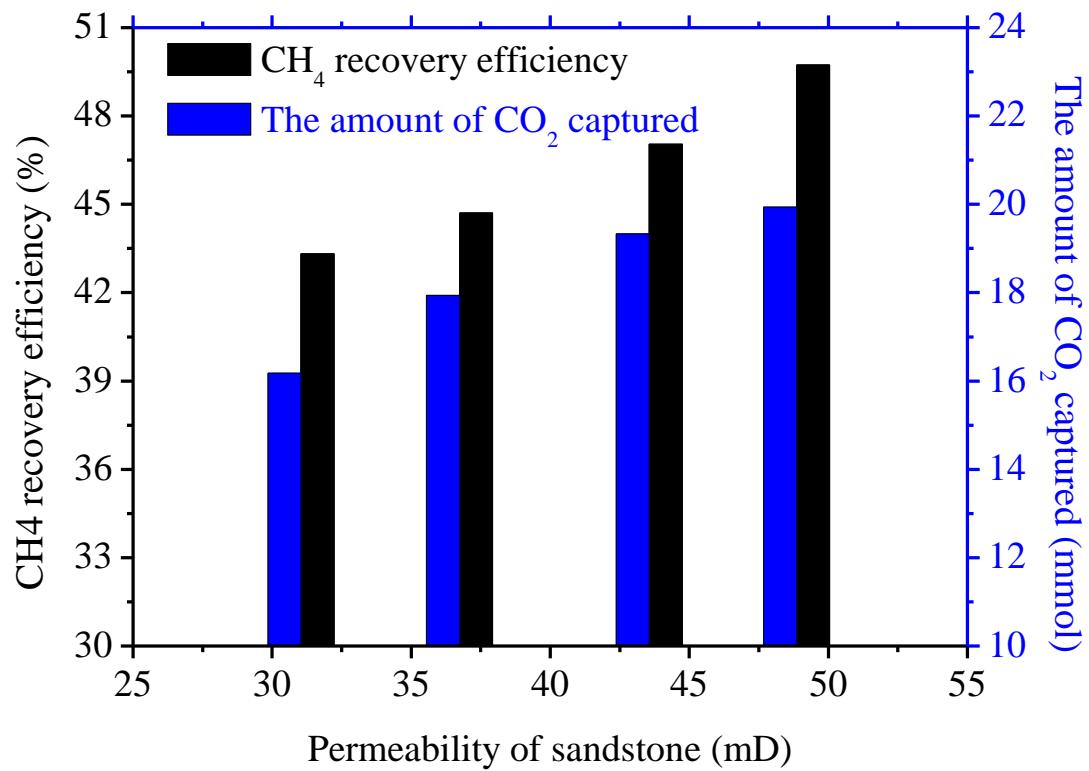


Figure 8. Methane recovery efficiency and the amount of CO₂ captured at different permeability of sandstones.

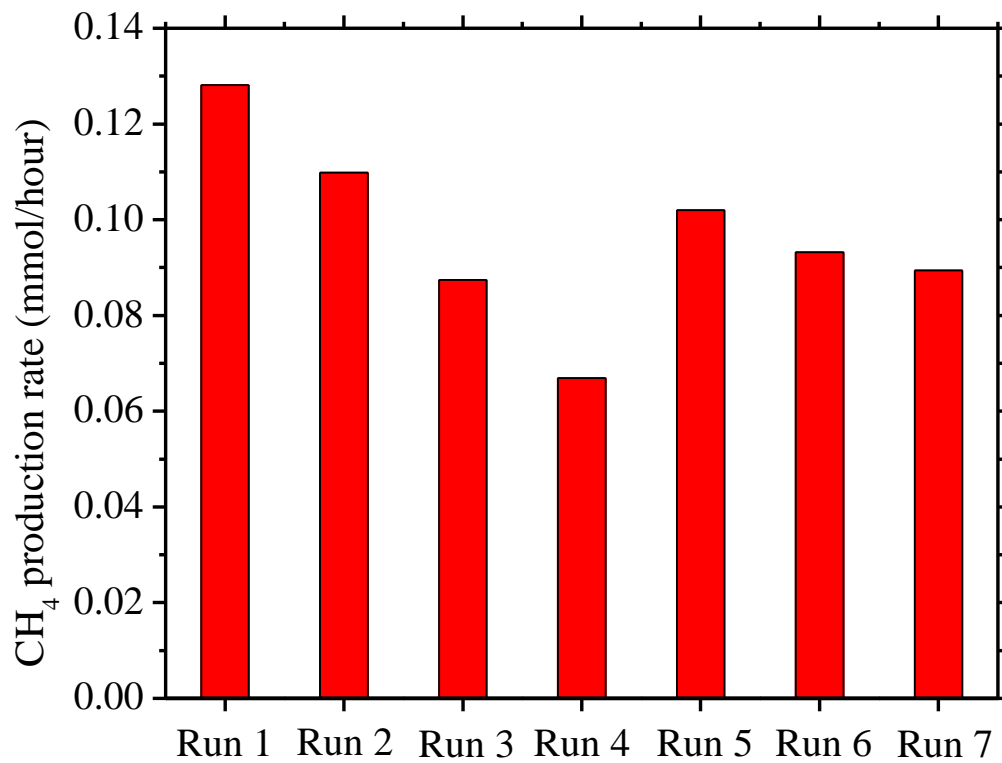
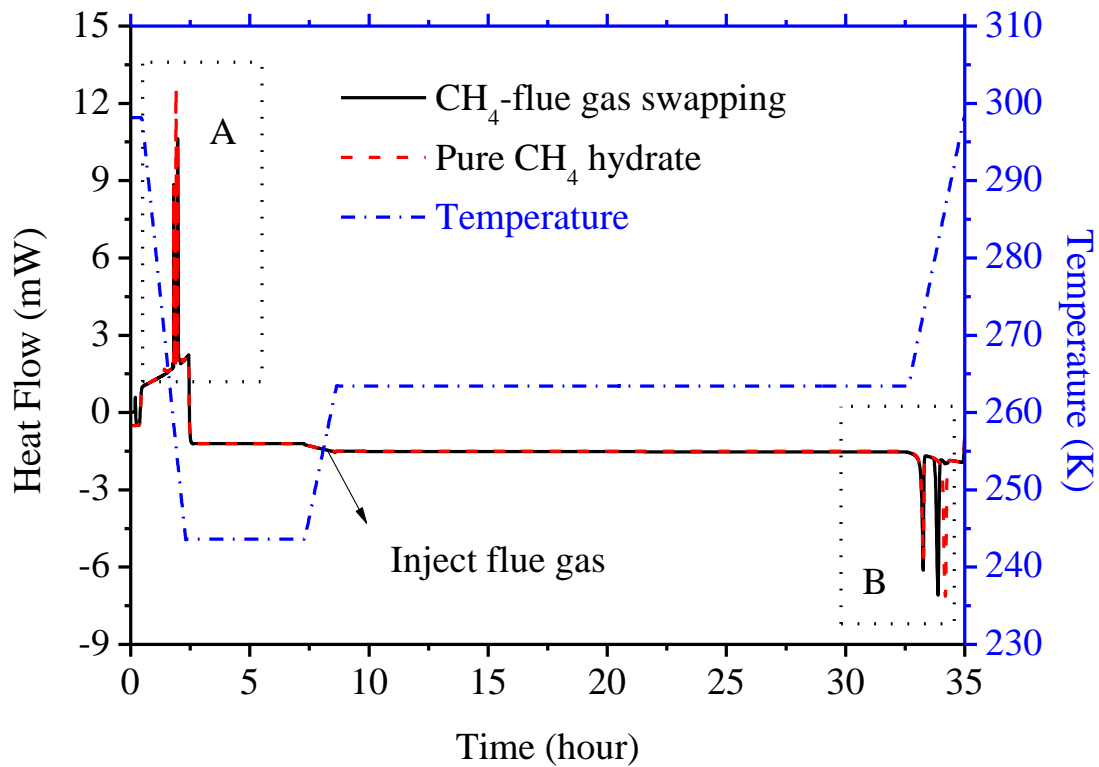


Figure 9. The average methane production rate in each experimental run.

3.4. Reaction heat investigation of CH₄-flue gas swapping with DSC apparatus.



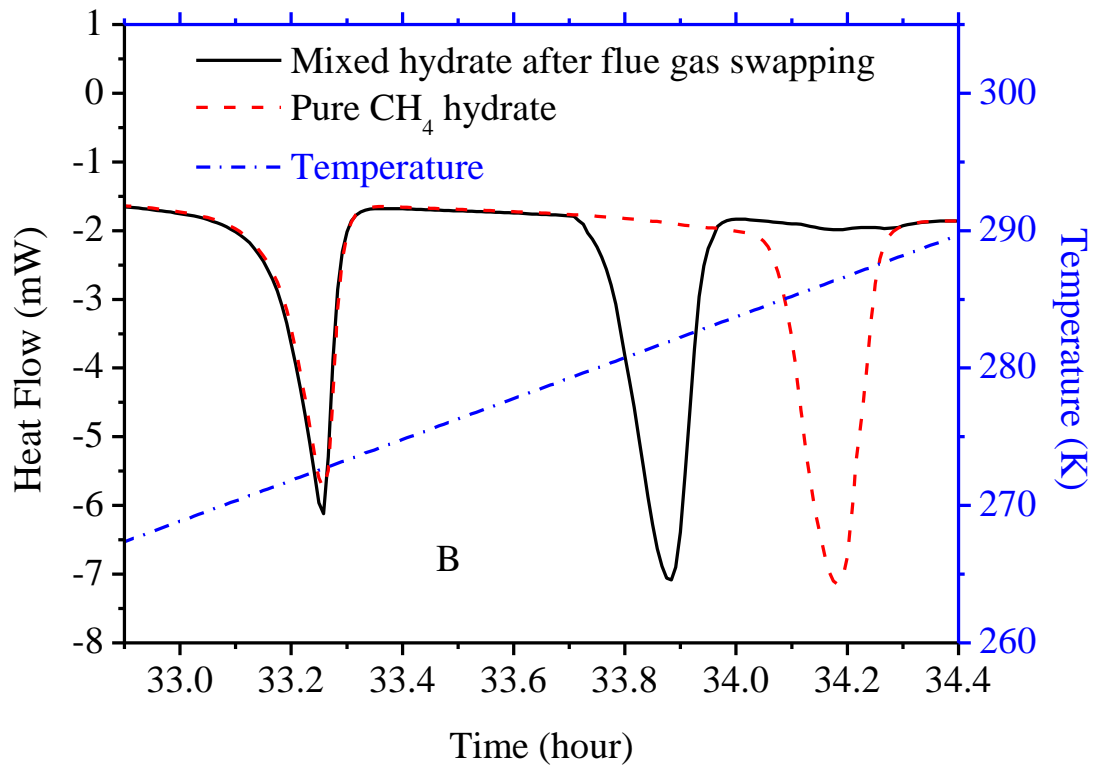
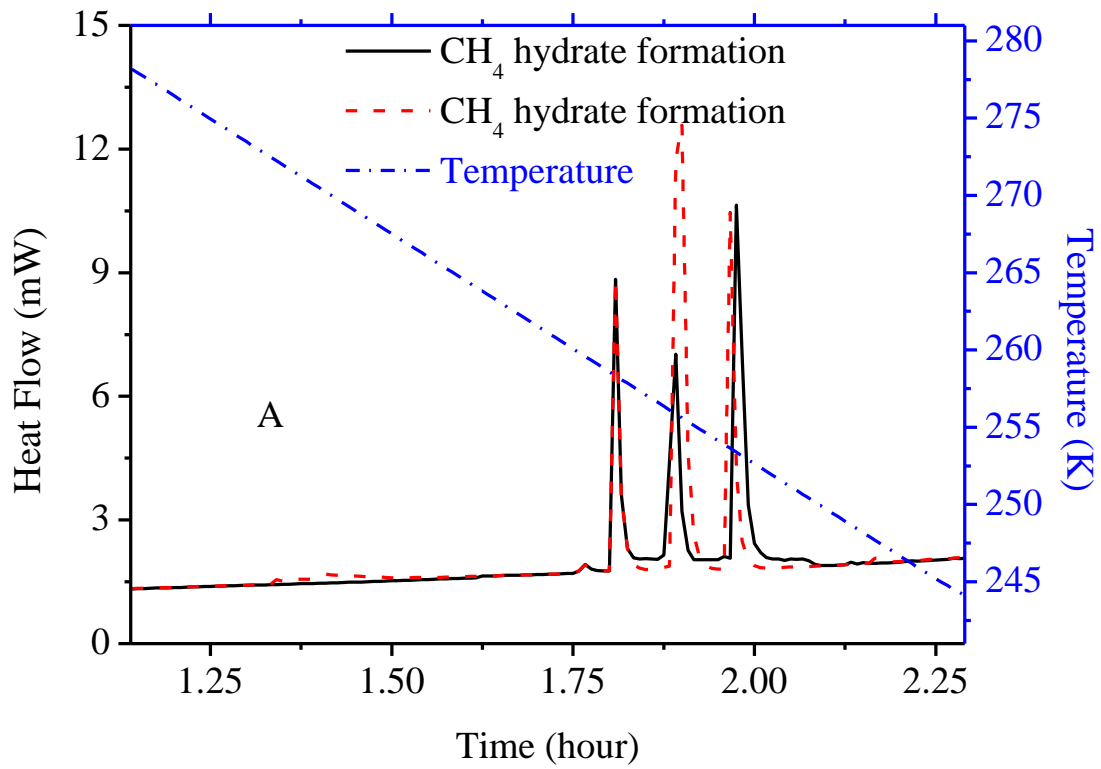


Figure 10. Heat flow changes in brine obtained during methane hydrate formation (A), flue gas swapping and dissociation (B).

In this study, it was observed that the reaction rate of CH₄-flue gas swapping is low, and we infer that the reaction process was mainly controlled by mass transfer, because CO₂ molecules would diffuse along its concentration gradient in the hydrate-bearing sandstones and penetrate the already formed CO₂ hydrate outer layer to reach the unreacted CH₄ hydrate. For studying whether the heat transfer would affect the CH₄-flue gas swapping, a micro differential scanning calorimetry (μ -DSC) was used to test the whole process. Three capillary tubes loaded with around 3.0 mg salt water (3.35 wt% NaCl) were placed inside the sample cell, the temperature procedure as follows: first, cooling from 298.15 K to 243.15 K at 0.5 K·min⁻¹, then keeping constant at 243.15 K for 5 hours after which heating from 243.15 K to 263.15 K at 0.25 K·min⁻¹, subsequently, injecting flue gas and keeping constant at 263.15 K for 24 hours after that heating to 293.15 K at 0.25 K·min⁻¹ to dissociate the hydrate. The specific operation of μ -DSC experiments can refer to our previous study.⁴² One thing to note is that, in order to prevent hydrate dissociation when releasing the free CH₄ gas and injecting with flue gas, the sample cell pressure should be maintained slightly higher than the hydrate equilibrium pressure at 263.15 K. Figure 10 shows the heat flow curves in CH₄ hydrate formation, flue gas swapping and hydrate dissociation at 9.0 MPa. The three exothermic peaks in cooling cycle indicated CH₄ hydrate formation (Figure 10 A), the reason of forming more than one exothermic peak might be that the capillary tubes are separated and the nucleation cannot affect each other. The endothermic peak at 273.15 K in heating cycle suggests ice melting and another denotes hydrate dissociation. No peaks detected in the CH₄-flue gas swapping and the heat flow changes are constant, which demonstrated the CH₄-flue gas swapping proceeds without significant exothermic or endothermic phenomenon. It can be inferred that the CH₄ hydrate structure might not be completely destroyed or collapsed in the CH₄-flue gas swapping, and CO₂ molecules are likely to take the place of CH₄ molecules in a peaceful way in the hydrate cage. In heating cycle, the endothermic peak of the mixed hydrates after swapping present a distinct shift

with that of pure CH₄ hydrate, which suggests the hydrate phase composition has changed remarkably. The reason might be CO₂ molecules have already replaced a portion of CH₄ molecules in hydrate cage and formed (CO₂+CH₄) mixed hydrates, the new formed hydrates showed different dissociation temperature and endothermic peak position at the same pressure and heating rate.

Based on our investigation in this study and previous research results in literature,⁴³⁻⁴⁸ we infer the mechanism on CH₄-flue gas swapping as follows: Firstly, the CO₂ molecules will destroy the stability of methane hydrate structure due to the difference of chemical potential, especially the large cages in sI hydrate will be firstly destabilized under the action of CO₂ molecules. Some researchers believed that the destroyed cages are mainly large (5¹²6²) cages, while small (5¹²) cages can be maintained for a longer time, because large cages have some unfavorable angles of H₂O molecules for the planar hexagonal rings.^{49,50} Secondly, the large cages will distort and the CH₄ molecules trapped inside are released. It should be noted that this process will leave plentiful hydrate residual rings which retain most of the hydrogen bonding energy and facilitate the process of CO₂ molecules being trapped in hydrate cages and enhancing the dynamic process. In addition, this is also the reason that we did not observe obvious endothermic and exothermic peaks in the process of swapping by μ -DSC test. Finally, the small cages will be unstable and liberate CH₄ molecules while being filled with N₂ molecules after most CO₂ molecules have been enclosed in the large cages. It can be concluded that the CH₄-flue gas in hydrate-bearing sandstones is mainly influenced by mass transfer since there is no significant heat phenomenon in the swapping process, larger porosity and permeability of sandstones will be beneficial to methane production using swapping method. However, this doesn't mean that the factors involving heat transfer is not worth considering in the swapping process, Zhao et al.⁵²⁻⁵⁴ did a series of studies on CH₄ recovery from gas hydrate by depressurization, nitrogen injection as well as CO₂ swap method, they believed that the sensible heat of the reservoir and ambient heat transfer have a significant influence on hydrate

dissociation. Therefore, the investigation of mechanism of CH₄-flue gas swapping is an on-going process of great significance, in which both experimental and simulation studies are necessary in the future research.

4. Conclusions

A core flooding setup was used to test CH₄ recovery from artificial hydrate-bearing sandstones by injecting simulated flue gas. Seven experimental runs were performed to examine the influence of hydrate saturation as well as the initial porosity and permeability of sandstones on methane production and carbon dioxide capture. The experimental results indicated that the CH₄ recovery efficiency and the amount of CO₂ captured increase with the increased hydrate saturation at the identical initial porosity and permeability of sandstone. The highest CH₄ recovery efficiency obtained here is 51.6% at 9.2 MPa and 277.15 K under the condition of hydrate saturation of 82.5% with the initial porosity and permeability of sandstone are 25.1% and 49 mD, respectively, while 99.4% of CO₂ in simulated flue gas is sequestered in the hydrate phase after swapping. With increasing initial porosity and permeability of sandstone, the CH₄ recovery efficiency and the amount of CO₂ captured increase at the same hydrate saturation and reaction time. For exploring the swapping mechanism of CH₄-flue gas, a high pressure μ -DSC apparatus was used to test the heat changes in the whole reaction, no obviously thermal phenomenon were observed in the CH₄-flue gas swapping, which indicated that CH₄ hydrate would form mixed hydrates directly instead of undergoing a dissociation and reformation procedure. Based on the observed experimental results, the CH₄-flue gas swapping mechanism was proposed: firstly, the hydrate cage would be distorted to release CH₄ molecules, and the hydrate residual cage structure can promote CO₂ hydrate nucleation and enhance its dynamic process. With the swapping proceeding, the outer layer hydrate slows down the mass transfer and CH₄-flue gas swapping rate. In addition, the decrease of porosity and

permeability of sandstones reduces the diffusion rate of CO₂ along concentration gradient from outer layer to inner layer, making it more difficult for CO₂ molecules to reach the unreacted CH₄ hydrate. It is concluded that the CH₄-flue gas swapping process was essentially controlled by mass transfer in sandstones.

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